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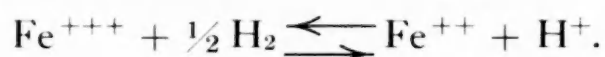
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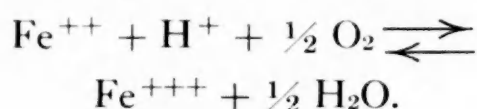
Oxidation-Reduction Indicators

IN CHEMICAL literature, the term reduction is applied to two types of reaction for which the following may be cited as examples: (1) the reduction of ethylene to ethane; (2) the reduction of ferric chloride to ferrous chloride.

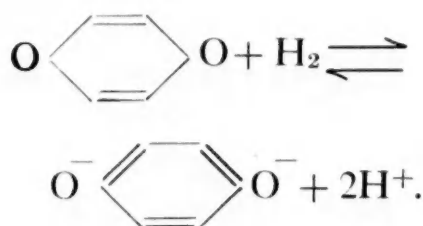
The first involves the taking up of a neutral molecule by a neutral molecule, but the second involves a change in the charge on an ion. This is made clear by means of the skeleton equation of the second reaction:



To emphasize the oxidation character of the reverse reaction, it may be written:



Since the reaction involves ions, it has been possible to measure its free energy as a potential at an electrode, and such potentials are listed together with the single potentials of the metals, for example. The oxidation-reduction characteristics of many organic reactions are similarly susceptible of measurement electrically. The reduction of quinone is a familiar case:



It should be noted that here also, as in the case of Fe^{+++} , reduction involves hydrogen ion and that, therefore, the complete equation for the potential must include a term depending on hydrogen ion concentration. The equation takes the form:

$$E_h = E_o - \frac{RT}{2F} \ln \frac{[S_r]}{[S_o]} +$$

$$\frac{RT}{2F} \ln [K_1 K_2 + K_1 \text{H}^+ + \text{H}^{+2}]$$

Here E_h is the observed potential relative to the normal hydrogen electrode; $[S_r]$ and $[S_o]$ are, respectively, concentrations of reductant and oxidant; K_1 and K_2 are the ionization constants of the two acid groups of the hydroquinone; and E_o is a characteristic constant of the system. For other oxidation-reduction systems, the third term may be more or less elaborate, depending on the number of acid (or basic) ionization constants involved. When the ratio of oxidant to reductant is made unity, the measurement of E_h may obviously be used to determine pH. If the pH is held constant with a buffer solution or is determined independently, from E_h can be calculated the ratio of oxidant to reductant in the system.

In the measurement of pH it is often impossible or inconvenient to use the electrical method to determine the

hydrogen ion concentration, and indicators are used instead. In other words, to the system is added a small amount of an acid or base which is colored in the acidic or basic form, or both. The fractional transformation of the indicator, if one knows its ionization constant, permits the calculation of the hydrogen ion concentration of the unknown solution. Similarly, in the determination of the oxidation or reduction intensity of an unknown system, it is possible to use indicators which, in this case, suffer their color transformation in going from an oxidized to a reduced state.

As in the case of hydrogen ion indicators it is necessary to know the ionization constant of the acid, so with oxidation-reduction indicators, one must know the oxidation-reduction potential, and, as an extra requirement, the pH of the system. Knowing these, from the fractional color transformation of the indicator, it is possible to calculate the oxidation-reduction intensity of the system. Unfortunately, a complete series of indicators, covering the range from the oxidizing intensity of oxygen to the reducing intensity of hydrogen, has not been investigated, but an appreciable portion of the field has been covered, chiefly by W. M. Clark and his co-workers. The included table gives a list of indicators with their normal reduction potentials, and included are a few inorganic reduction potentials for comparison. The values are given for pH 7 for the sake of uniformity.

TABLE

<i>Substance (Oxidant)</i>	<i>Potential</i>
Indigo disulphonate	-0.125
Indigo trisulphonate	- .081
Indigo tetrasulphonate	- .046
Methylene Blue	+ .011
Toluylene Blue	+ .115
1-Naphthol-2-sulphonate- indo-3-5-dichlorophenol	+ .119
1-Naphthol-2-sulphonate- indophenol	+ .123
2,6-dichlorophenolindo- o-cresol	+ .181
2,6-dichlorophenolindo- phenol	+ .217
Bindschedler's Green	+ .224
o-Chlorophenolindophenol	+ .233
m-Bromphenolindophenol	+ .248
Hydrogen	- .42
Benzo-quinone	+ .30
Fe ⁺⁺⁺	+ .75
Fe(CN) ₆ ⁻⁻⁻⁻	+ .40
Sn ⁺⁺⁺	+ .20

The use of indicators in the determination of acidity has become very general in the last few years. To the biologist and physiologist, the question of oxidation-reduction intensity has appeared of similar importance, and the greater amount of the necessary study of the indicators has been made by such workers. That the technic is not restricted to these fields is indicated by the fact that recently it has been applied to the investigation of such various materials as soils, wines, cheese, gasoline anti-knock compounds, etc.

Chemiluminescence Demonstrations

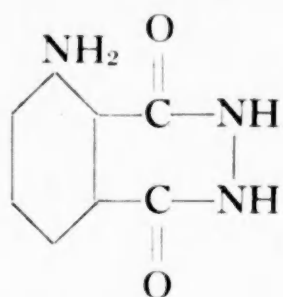
ONE of the most beautiful and striking demonstrations for laboratory or lecture work is that of chemiluminescence or "cold light." Certain chemical reactions, usually ones involving the oxidation of an organic compound, result in the development of light without other visible reaction. Even heat,

which is usually associated with light of any kind, is noticeably absent.

This phenomenon of chemiluminescence has long been known, but has not previously been employed extensively because of difficulties encountered in the available reactions. These were complex and dangerous, produced only

a limited luminescence, or required reagents not readily obtainable. But now, through the addition to the list of Eastman Organic Chemicals of 3-Aminophthalhydrazide, there has been made available a compound which overcomes all of these objections. The reaction is simple, safe, and develops light of intense brilliancy.

As an enolic compound, 3-Aminophthalhydrazide contains two labile hydrogens. In the ketonic form, it has the following structural formula:



The name "luminol" has recently been applied to this compound in place of its strictly chemical name for convenience, to associate with it the property of luminescence, and to denote its enolic character.

The demonstration requires only the oxidation of 3-Aminophthalhydrazide in dilute alkaline solution with 3% alkaline hydrogen peroxide and a second oxidizing agent. All four components are necessary in the solution to obtain the strongest radiation. Almost innumerable variations can be used in the actual procedure, from the mere mixing of the required chemicals to very elaborate displays. A few of the simpler methods are given to serve as guides.

For small audiences or laboratory demonstrations, the flask method is the most satisfactory. In a two-liter long-necked flask, 0.2 gram of 3-Aminophthalhydrazide is dissolved in 20 cc. of 5% sodium hydroxide and diluted to 2 liters with water. In a similar flask, 0.5 gram of potassium ferricyanide is dissolved in water, 20 cc of 3% hydrogen peroxide added and diluted to 2 liters with water. When both solu-

tions are ready and the room is darkened, one flask is grasped in each hand and the contents of them poured simultaneously through a funnel into a six-liter flask. The reaction starts as soon as the liquids mix in the funnel. After the initial development of the light has begun, the flask is swirled and a small quantity of solid potassium ferricyanide added. The brilliance is increased and can be still further intensified by the gradual addition of 5% sodium hydroxide. At the concentrations given, the original light intensity is small, but the increased brilliance obtained by the addition of further reagents is very beautiful.

For demonstration to larger audiences, it is more convenient to use a large jar containing about 14 liters of water. In a small flask is dissolved 1.0 gram 3-Aminophthalhydrazide in 100 cc. of 5% sodium hydroxide, and, in a second flask, 2.5 grams of potassium ferricyanide in 100 cc. of 3% hydrogen peroxide. To indicate more clearly the lack of heat in the reaction, the solutions may be poured simultaneously over a cake of ice which has been floated in the water. The solutions should be allowed to mix in concentrated form on the ice before being diluted with the surrounding water. After the reaction mixture has diffused throughout the water, the solution is stirred vigorously with a glass rod and further potassium ferricyanide or alkali or both added as desired.

A very beautiful display may be prepared by means of two fine sprays, which are made to intersect some distance above the lecture table. Each spray or humidifier is connected to a compressed air source and to one of the stock solutions previously mentioned. Care should be taken that the spray guns are operating at the same rate. By variation of the stock solutions, the resulting mist can be changed from a hardly visible cloud to a brilliant fountain resembling a display of fireworks.

Eastman Organic Chemicals as Analytical Reagents

XXXVI REAGENTS FOR CHLORINE

O-TOLIDINE

STANDARD METHODS OF WATER ANALYSIS, 6th Ed. (1925)

For the determination of chlorine in water, 1 cc. of a 0.1% solution of o-tolidine in dilute hydrochloric acid is mixed with 100 cc. of the sample to be tested and the solution allowed to stand for at least 5 minutes. The color varies from yellow to orange, proportional to the amount of free chlorine present. For quantitative estimation, the color is compared to standards prepared from solutions of copper sulfate and potassium dichromate.

The reagent is not specific but gives similar reactions with certain other types of compounds. Therefore, care must be exercised in interpreting results.

DICHLOROFLUORESCEIN

Kolthoff, Lauer, and Sunde, J.A.C.S., 51, 3273 (1929)

For argentometric titration of chlorides in dilute as well as in weakly acid solutions, dichlorofluorescein is a suitable internal indicator. When chloride ions are titrated with silver nitrate, the silver chloride absorbs silver ions at the equivalence point or slightly beyond. This "silver body" then absorbs fluorescein ions from the solution, resulting in dark red silver fluoresceinate on the surface of the precipitate.

In practice, 2 drops of indicator solution are added for every 10 cc. of chloride solution to be tested and the titration started with silver nitrate. The silver chloride remains in colloidal solution until about 0.5% before the equivalence point when it flocculates. The titration is conducted carefully and at the end point the silver chloride suddenly turns dark red.

NITROSODIMETHYLANILINE

Yoe, PHOTOMETRIC CHEMICAL ANALYSIS, VOL. I, p. 163

Perchlorates may be determined by means of the violet color formed by reaction with nitrosodimethylaniline. The reagent is prepared by dissolving one gram of the dry chemical in alcohol and diluting to one liter.

A one-gram sample of the unknown is dissolved in 25 cc. of water, and 2 cc. of the reagent added. The solution is mixed and allowed to stand for several hours. The color formed is compared to standards run concurrently. The standard perchlorate solution may be prepared by dissolving 0.1393 gram potassium perchlorate in water and diluting to one liter. When 10 cc. of this standard are diluted to 100 cc., the resultant solution contains 0.01 mg. of perchlorate per cubic centimeter. Iodates and periodates do not interfere but iodides must be removed with silver oxide.

SODIUM NITROPRUSSIDE

Kolthoff and Furman, VOLUMETRIC ANALYSIS, VOL. II, p. 260

As an indicator for the mercurimetric titration of chloride, sodium nitroprusside has been found very satisfactory. For every 10 cc. of liquid to be tested, 0.1 cc. of a 10% solution of sodium nitroprusside is added and the solution titrated with 0.1 N mercuric nitrate until a permanent turbidity is obtained. The mercuric nitrate solution is prepared by dissolving the commercial salt or pure mercuric oxide in nitric acid and water. It is standardized against pure sodium chloride. In these titrations, it is necessary to correct the result for a titration error in accordance with tables given by the authors.